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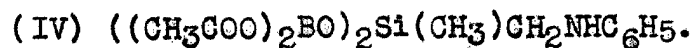
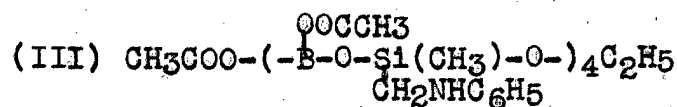
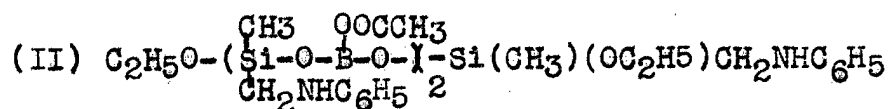
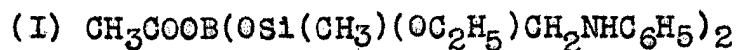
The Synthesis of Borosiloxane Oligomers and their Resistance to Hydrolysis

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Polymers with inorganic units in the molecular chains have considerable practical importance. Parallel with the development of the polyorganosiloxanes (themselves) attention was soon drawn to those polymers set up with main bonds holding boron, in addition to silicon and oxygen.

Organoborosiloxanes easily (undergo) hydrolysis in water. The explanation lies in the high degree of polarity of the bonds B-O-Si and the ability of boron easily to utilize p orbitals forming bonds coordinating with nucleophilic reagents. Present interest stems from the question as to whether the bonds B-O-Si are always stable with regard to water. Such stability (resistance) could probably be heightened by the introduction as a side chain to the inorganic chain, a group containing nitrogen, intended to furnish a coordinating bond to the boron, utilizing this pair of electrons.

For this purpose there were synthesized four oligomers with phenylaminomethyl groups on a silicon atom as indicated:

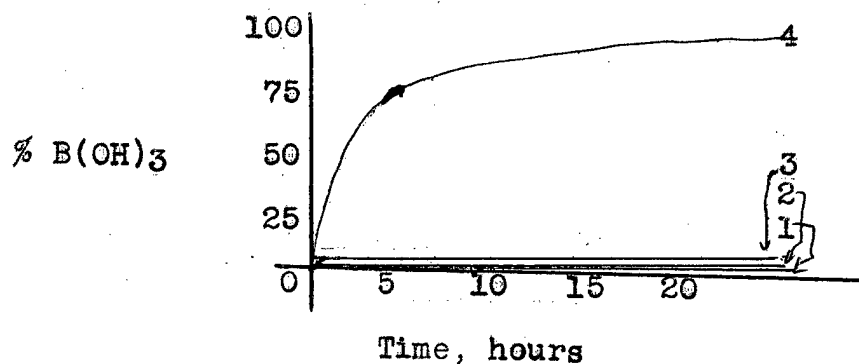


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Structures of the chain groups and side chains were determined according to the customary chemical methods and confirmed by infrared data. These compounds showed frequencies of B-O-Si,  $1345\text{ cm}^{-1}$ , CH<sub>3</sub>-Si,  $820-800\text{ cm}^{-1}$  and  $1282-1250\text{ cm}^{-1}$ . The hydrolytic resistance of the B-O-Si linkage in these oligomers is defined at room temperature by the amount of boric acid formed in water solution from a known amount of the substance, immersed in water.

	Solubility	Viscosity	Brittle Pt
I	C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> COCH <sub>3</sub> , O(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O, CH <sub>3</sub> COOH	0.15	-35°
II	as I	0.20	-12°
III	C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> COCH <sub>3</sub>	0.21	+50°
IV	as I	0.07	+44°

On the curve (below) is the evidence of definite hydrolytic resistance (on the part) of the oligomers prepared. As seen, from the runs, on the curve, the hydrolytic resistance of all four compounds was tested.



Comparison of the hydrolytic resistance in the compounds studied with their structures shows that the influence of the phenylaminomethyl group on the hydrolytic resistance of B-O-Si is manifested strongly in each case where the number of phenylaminomethyl groups is sufficient to coordinate with (all of) the boron atoms. However, when the number of boron atoms exceeds the number of phenylaminomethyl groups, as will be seen in compound IV, the stabilizing effect of the phenylaminomethyl groups is not operative.

#### Experimental Part

Boron triacetate was prepared by the method of Andrianov and Volkova (2) with m.p. 130°-131°. Methylphenylaminomethyldiethoxysilane, b.p. 145°-147° (12 mm-13 mm),  $n_{D(20^{\circ})}$  1.4981,  $d_{(20^{\circ})}$  1.006.

Synthesis of Oligomer II. In a flask furnished with an upright condenser and measuring flask, with receiving flask, were placed 18.80 g. (0.1 mole) of boron triacetate and 47.88 g. (0.2 mole) of methylphenylaminomethyldiethoxysilane. The contents of the flask were heated to 145° C., then discontinued to distill off ethyl acetate (94% of theory) (followed by) vacuum distillation of the reaction product over a four hour (period) (50° C. at 20 mm.)

Found: %, N - 5.87; B- 2.21, 2.25; Si- 11.58, 11.82;  
 $C_{22}H_{35}O_6N_2SiB$  - 18.57, 17.84;  $C_{22}H_{35}O_6N_2SiB$ .  
 Calculated; %, N- 5.70; B- 2.21; Si- 11.46;  $C_2H_5O$ - 18.35.

The synthesis of each oligomer was carried out under analogous conditions with the proper molar ratio of boron triacetate and methylphenylaminomethyldiethoxysilane.

Hydrolytic resistance was determined by methods given by Andrianov and Volkova (2).

In the Table are presented the characterization of these oligomers.

#### Summary

1. The synthesis of borosiloxy oligomers containing the phenylaminomethyl group attached to a silicon atom.

2. A study of resistance to hydrolysis of the borosiloxy oligomers and evidence that (these) oligomers with various phenylaminomethyl groups in equal number to the boron atoms in the molecule or greater, possess ample resistance to hydrolysis. Oligomers with boron atoms in excess than the number of phenylaminomethyl groups are hydrolytically unstable.

#### Bibliography

1. M. Wick, Kunststoffe, 50 433 (1960)
  2. K.A. Andrianov and L.M. Volkova, Izvestiya Akademii Nauk, SSSR, OKhN, 303 (1957)
  3. K.A. Andrianov, V.S. Tikhanov, L.M. Khananashvili, En-Tsze Han and Shu-Yu Han, Plasticheskie Massy, (No. 12) 25 (1962)
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